

Patents Act 1977 Examiner's report to the Comptroller under Section 17 (The Search report)	Application number GB 9413192.7
Relevant Technical Fields (i) UK Cl (Ed.N) C5D DHC, DHZ, DHX (ii) Int Cl (Ed.6) C11D 3/382 C11D 3/39 Databases (see below) (i) UK Patent Office collections of GB, EP, WO and US patent specifications. (ii) ONLINE DATABASE WPI	Search Examiner M ELLIOTT Date of completion of Search 26 OCTOBER 1994 Documents considered relevant following a search in respect of Claims :- 1 TO 11

Categories of documents

X: Document indicating lack of novelty or of inventive step.	P: Document published on or after the declared priority date but before the filing date of the present application.
Y: Document indicating lack of inventive step if combined with one or more other documents of the same category.	E: Patent document published on or after, but with priority date earlier than, the filing date of the present application.
A: Document indicating technological background and/or state of the art.	&: Member of the same patent family; corresponding document.

Category	Identity of document and relevant passages	Relevant to claim(s)
A	US 4879057 A (DEGUSSA AG) whole document	1 at least
A	US 4992194 A (LEVER BROS) whole document	1 at least

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11. A method for cleaning and bleaching fabrics in the wash by contacting the fabrics with a dilute solution formed from an effective amount of an aqueous liquid detergent composition according to any of Claims 1 to 10.

4. A stable, pourable aqueous liquid laundry detergent composition according to any of Claims 1 to 3 which comprises from 1.5% to 5% of monononanoylamido peroxyadipic acid.
5. A stable, pourable aqueous liquid laundry detergent composition according to any of Claims 1 to 4 which comprises from 5% to 30% of a pH adjusting system comprising:
 - a) a borate and;
 - b) a polyol wherein the polyol is a cis-1,2 polyol capable of forming a complex with the borate when the composition is in a concentrated form to cause a reduction in pH of the composition to a value of 3-6 and the complex being capable upon dilution of the composition, of dissociating in dilute solution to liberate the borate to cause an increase in pH in the solution to a value of 7-10, the polyol to borate weight ratio being 1:1 to 10:1.
6. A stable, pourable aqueous liquid laundry detergent composition according to any of Claims 1 to 5 which comprises from 1% to 20%, by weight of the composition, of a boron compound selected from borax, boric oxide, sodium orthoborate and sodium pyroborate; and from 1% to 20%, by weight of the composition, of a polyol selected from sorbitol, dulcitol, xylitol, xarabitol, manitol, fructose, galactitol, catechol, pinacol, glucose and polyhydroxy fatty acid amide.
7. A stable, pourable aqueous liquid laundry detergent composition according to any of Claims 1 to 6 which further comprises from 1% to 3%, by weight of the composition, of C₁₀₋₁₂ fatty acid.
8. A stable, pourable aqueous liquid laundry detergent composition according to any of Claims 1 to 7 which comprises from 3% to 6%, by weight of the composition, of borax and from 10% to 15%, by weight of the composition, of sorbitol.
9. A stable, pourable aqueous liquid laundry detergent composition according to any of Claims 1 to 8 which further comprises from 0.05% to 0.5% of ethylhydroxydiphosphonate.
10. A stable, pourable aqueous liquid laundry detergent composition according to any of Claims 1 to 9 which contains no enzymes and which further comprises an effective amount of detergency builder.

Claims

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1. A stable, pourable aqueous liquid laundry composition characterized in that said composition contains, by weight of the composition';

- a) from 1% to 30%, preferably 1% to 20%, of solid, substantially water-insoluble organic peroxyacid;
- b) from 10% to 40%, preferably 15% to 30%, of detergent surfactant selected from anionic surfactants and mixtures of anionic and nonionic surfactants with a ratio of nonionic to anionic that is not greater than 1:1;
- c) from 2% to 40%, preferably 10% to 25%, of a pH jump system which produces a pH in the composition of between 3 and 6, preferably between 3.5 and 5, and which, upon dilution of the composition, produces a pH of between 7 and 10, preferably between 7.5 and 9, in the dilute solution; and
- d) from 0.05% to 2%, preferably 0.1% to 1%, of agar or xanthan polysaccharide;

said laundry detergent composition being further characterized in that it does not comprise a stability enhancing-polymer which is a copolymer of a hydrophobic and hydrophilic monomer; and

in that said laundry detergent composition has a viscosity of from 100 to 3000 cps, preferably from 300 to 1000 cps, more preferably from 400 to 900 cps, at 20°C when measured with an RVT Brookfield Viscometer, using a No. 3 spindle and a setting of 100 rpm.

2. A stable, pourable aqueous liquid laundry detergent composition according to Claim 1 which comprises from 1% to 20% of solid, substantially water-insoluble organic peroxyacid selected from 4-nonylamino-4-oxoperoxybutyric acid; 6-nonylamino-6-oxoperoxyhexanoic acid, heptyl sulfonylperpropionic acid; decylsulphonyl perpropionic acid; heptyl-, octyl-, nonyl-, and decylsulphonylperbutyric acids; 1,12-diperoxydodecanedioic acid; and phthaloyl aminoperoxy-caproic acid.

3. A stable, pourable aqueous liquid laundry detergent composition according to Claim 1 or Claim 2 which comprises from 30% to 70%, preferably 40% to 60%, by weight of the composition, of distilled, deionized water.

	Sorbitol	20
	Borax	5.0
	Lauric acid	2.0
	Xanthan gum	0.15
5	Sodium polyacrylate (MW 4,500)	0.20
	FWA	0.20
	Sodium hydroxide (4N)	to pH 4.5
	Water	<u>Balance</u>
	TOTAL	100
10	Viscosity: 910 centipoise (cps)	
	pH Jump: 4.5 (product) to 7.95 (wash)	

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WHAT IS CLAIMED IS:

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	<u>Ingredient</u>	<u>Active %</u>
	C12-13 alkylethoxylate (E6-5)	15
	Linear alkylbenzene sulfonic acid	5.2
	1,12-Diperoxydodecanedioic acid	2
5	Dipicolinic acid	0.3
	Magnesium sulfate heptahydrate	4.2
	Sorbitol	14.1
	Borax	5.1
	Lauric acid	2.0
10	Xanthan gum	0.12
	Sodium polyacrylate	0.25
	FWA	0.20
	Polyvinyl pyrrolidone (MW 4,500)	1.0
	Sodium hydroxide (4N)	to pH 4.5
15	Water	<u>Balance</u>
	TOTAL	100

Viscosity: 660 centipoise

pH jump: 4.5 (product) to 7.85 (wash)

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In the above formula, other peroxyacids can be substituted for the 1,12-diperoxydodecanedioic acid, such as monononylamido peroxyadipic acid or sulfone peroxyacid or phthaloyl amino-peroxycaproic acid. Agar polysaccharide can be substituted for the xanthan gum. Water can replace magnesium sulfate heptahydrate and sodium sulfate in the above formula.

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EXAMPLE IV

A composition of the present invention (high nonionic surfactant) is as follows. The procedure for preparation is as described in Example I.

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	<u>Ingredient</u>	<u>Active %</u>
	C12-15 alkylethoxylate (E9)	15
	C12 linear alkylbenzene sulfonic acid	6.4
35	Monononylamido peroxyadipic acid	2
	Ethylhydroxydiphosphonate	0.2
	Magnesium sulfate heptahydrate	6.0

EXAMPLE II

A composition of the present invention containing 1,12-diperoxydodecanedioic acid as the peroxyacid is as follows. The procedure for preparation is as described in Example I.

5	<u>Ingredient</u>	<u>Active %</u>
	C12-13 alkylethoxylate (E6.5)	12.1
	C12 linear alkylbenzene sulfonic acid	5.2
	1,12-Diperoxydodecanedioic acid	2
	Dipicolinic acid	0.3
10	Magnesium sulfate heptahydrate	6.8
	Sodium sulfate	5.38
	Sorbitol	10.6
	Borax	2.4
	Lauric acid	2.5
15	Xanthan gum	0.12
	Sodium polyacrylate (MW 10,000)	0.1
	FWA	0.1
	Polyvinyl pyrrolidone (MW 10,000)	1.0
	Sodium hydroxide (4N)	2.0
20	Water	<u>Balance</u>
	TOTAL	100

Viscosity: 430 centipoise

pH jump: 4.5 (product) to 7.78 (wash)

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In the above formula, other peroxyacids can be substituted for the 1,12-diperoxydodecanedioic acid, such as monononylamido peroxyadipic acid or sulfone peroxyacid or phthaloyl amino-peroxycaproic acid. Agar polysaccharide can be substituted for the xanthan gum. Other detergent surfactants can be substituted for the above. Water can replace magnesium sulfate heptahydrate and sodium sulfate in the above formula.

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EXAMPLE III

A composition of the present (high nonionic surfactant) invention containing 1,12-diperoxydodecanedioic acid as the peroxyacid is as follows.

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The procedure for the preparation of the above composition containing peroxyacid bleach is as follows:

1. Xanthan gum is dissolved in enough water to make a 1% solution.
- 5 2. A pH jump premix is prepared by dissolving the sorbitol and borax in an equal amount of water. If any electrolytes are in the composition, they can also be dissolved in the pH jump premix.
- 10 3. The composition is prepared in an appropriate size beaker (typically a 2-liter beaker). First charge the beaker with the linear alkyl benzene sulfonic acid, alkylethoxylate and, if present, lauric acid, and mix to dissolve.
- 15 4. The pH jump premix is added to the stirring surfactant mix.
5. The chelant is added with agitation.
6. The desired amount of solid peroxyacid (e.g. NAPAA) is added and dispersed.
7. The xanthan gum solution is added.
- 20 8. Next the sodium polyacrylate is added.
9. Then the fluorescent whitening agent, and PVP, if present, is added.
10. The resulting mix is homogenized on a homogenizer at low speed for about 1 minute.
- 25 11. The pH of the composition is adjusted to 4.5 with a 4N sodium hydroxide solution.

The resulting product is a pourable, creamy suspension. The pH jump capability of the composition is checked by diluting 1.5 gm. of the composition into 1,000 gms. of water.

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In the above formula, other peroxyacids can be substituted for the monononylamido peroxyadipic acid, such as 1,12-diperoxy-dodecanedioic acid or sulfone peroxyacid or phthaloyl aminoperoxy-caproic acid. Agar polysaccharide can be substituted for 35 the xanthan polysaccharide. Other detergent surfactants can be substituted for the above. Water can replace magnesium sulfate heptahydrate and sodium sulfate in the above formula.

b. from about 10 to about 40% of C8-20 alcohol which has been ethoxylated with an average of from about 2 to about 20 moles of ethylene oxide per mole of alcohol;

5 c. from 0 to about 10% of bleach-compatible anionic surfactant; and

d. from about 2 to about 40% of a pH jump system which produces a pH in the composition of between about 3 and about 6, and upon dilution of the composition produces a pH of between about 7 and about 10 in the dilute solution;

10 e. from about 0.05 to about 2% of agar or xanthan polysaccharide; and

f. from about 0.5 to about 3% of C10-14 fatty acid.

The following examples illustrate the compositions of the present invention. All parts, percentages and ratios used herein
15 are by weight unless otherwise specified.

EXAMPLE I

A composition of the present invention is as follows.

	<u>Ingredient</u>	<u>Active %</u>
20	C12-15 alkylethoxylate (E9)	5.2
	C12-13 linear alkylbenzene sulfonic acid	12.1
	Monononylamido peroxyadipic acid	1.6
	Ethylhydroxydiphosphonate	0.2
	Magnesium sulfate heptahydrate	2.25
25	Sodium sulfate	2.25
	Sorbitol	10.5
	Borax	3.8
	Xanthan gum	0.10
	Sodium polyacrylate (MW 10,000)	0.15
30	Fluorescent whitening agent ("FWA")	0.30
	Sodium hydroxide (4N)	to pH 4.5
	Water	<u>Balance</u>
	TOTAL	100

35 Viscosity: 800 centipoise (cps)--pourable
pH jump: 4.38 (product); 8.00 (wash solution)

bisphosphonic acid) and other sequestering agents sold under the Dequest® trade name; and combinations of the above. Other sequestering agents for use herein are 2,6-pyridinedicarboxylic acid (dipicolinic acid), picolinic acid, and 8-hydroxyquinoline, and combinations thereof. From about 0.05 to about 0.5% of ethylhydroxydiphosphonate and dipicolinic acid, alone or combined, are preferred chelants.

The compositions herein may further contain magnesium sulfate, which is commercially available in the heptahydrate form. (If anhydrous magnesium sulfate is used, the above levels should be adjusted accordingly.)

The compositions may further contain sodium sulfate or potassium sulfate.

This invention further provides a method for cleaning and bleaching fabrics in the wash by contacting the fabrics with effective amounts of an aqueous liquid detergent composition comprising, by weight of the composition:

- a. from about 1 to about 30% of solid, substantially water-insoluble organic peroxyacid;
- b. from about 5 to about 50% of detergent surfactant;
- c. from about 2 to about 40% of a pH jump system which produces a pH in the composition of between about 3 and about 6, and upon dilution of the composition produces a pH of between about 7 and about 10 in the dilute solution; and
- d. from about 0.05 to about 2% of agar or xanthan polysaccharide; and which laundry detergent composition does not comprise a stability enhancing polymer which is a copolymer of a hydrophobic and a hydrophilic monomer.

Also provided is a method for cleaning and bleaching fabrics in the wash by contacting the fabrics with effective amounts of an aqueous liquid laundry detergent composition comprising, by weight of the composition:

- a. from about 1 to about 30% of solid, substantially water-insoluble organic peroxyacid;

R₂ is hydrogen or alkyl;

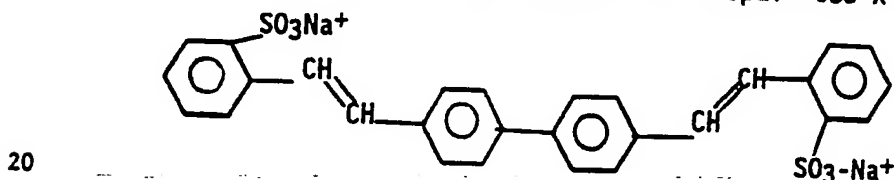
M is hydrogen, an alkali metal or ammonium ion;

n = 0-2, but the formula must contain at least one SO₃M group; and

5 m = 1-2 and when m=1, the substituent on the linkage carbon is hydrogen.

Suitable stilbene FWAs for use herein, if they are bleach-stable, are as described in U.S. Patents 4,309,316 and 4,298,490, Lange et al, issued January 5, 1982 and November 3, 1981, respectively, both incorporated by reference, and U.S. Patent 5,035,825, Eckhardt et al, issued July 30, 1991, also incorporated herein by reference.

The most preferred stilbene FWA for use herein, because it is bleach-stable, is Tinopal® CBS-X, which is benzenesulfonic acid, 2,2'-((1,1'-biphenyl)-4,4'-diyl-di-2,1-ethenediyl)bis-, disodium salt (CA Index Name). The formula for Tinopal® CBS-X is:



A sufficient amount of sodium hydroxide (0.4N) is added (usually 2-5 weight %) just before balancing with water to bring the pH of the composition at 20°C to a preferred pH of 4.5.

25 Hydrotropes such as sodium and potassium, xylene sulfonate, sodium and potassium toluene sulfonate, sodium and potassium sulfonate, and mixtures thereof, and related compounds (as disclosed in U.S. Patent 3,915,903, incorporated herein by reference) can be utilized in the compositions of the present invention. They may be present at levels of from about 0.5% to about 10%, preferably from about 1% to about 5%, by weight.

35 Examples of suitable chelants for use herein are: carboxylates, such as ethylene diamine tetraacetate (EDTA) and diethylene triamine pentaacetate (DTPA); polyphosphates, such as sodium acid pyrophosphate (SAPP), tetrasodium pyrophosphate (TSPP), and sodium tripolyphosphate (STPP); phosphonates, such as ethylhydroxydiphosphonate (Dequest® 2010 (1-hydroxyethylidene)

of the composition (to exclude the above-described low fatty acid levels).

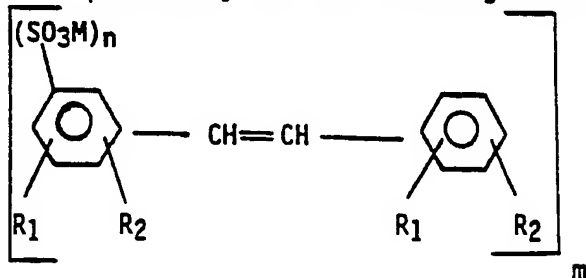
The compositions herein preferably have a viscosity of from about 100 to about 3000, most preferably from about 300 to about 1000, most preferably from about 400 to about 900, centipoise (cps) at 20°C when measured with an RVT Brookfield Viscometer, using a No. 3 spindle and a setting of 100 rpm. This viscosity is desirable for convenient pouring from a container by a liquid laundry detergent user.

G. Optional Ingredients

The ingredients herein should be combined in any manner which will evenly disperse or dissolve them in the composition, and which does not interfere with their action. The preferred order of addition is: surfactant, lauric acid, pH jump, electrolytes, chelant, peroxyacid, xanthan gum, polyacrylate, brightener, polyvinyl pyrrolidone and water to balance.

Optional and preferred ingredients include from about 0.5 to about 5, preferably from 1 to 2, % by weight of the composition of polyvinyl pyrrolidone (preferred) and/or polyvinyl alcohol. The PVP, which includes substituted and unsubstituted vinyl pyrrolidone polymerization products, and PVA have a molecular weight between about 4,000 and about 200,000, preferably between about 5,000 and about 100,000, most preferably between 10,000 and 30,000. A combination of PVPs and/or PVAs of different molecular weights could also be used.

Another optional and preferred ingredient is from about 0.05 to about 2, preferably from about 0.1 to 1, % by weight of the composition of bleach-stable, stilbene fluorescent whitening agent ("FWA"). This preferably has the following structural formula:



wherein R₁ is hydrogen, halogen, alkyl, alkoxy or phenyl;

concentrated solution. Upon dilution, the complex dissociates and yields borate ions, which have a buffered pH of about 9.

2. Other pH Jump Systems

5 Other pH jump systems aside from borate/polyol can be useful herein. These may include insoluble alkaline salts in product which dissolve in the wash for a more alkaline pH. These may include sodium carbonate, sodium bicarbonate, sodium silicate, sodium pyrophosphate and orthophosphate.

D. Xanthan polysaccharide

10 Compositions of the present invention comprise from about 0.05 to about 2%, preferably from about 0.1 to about 1%, most preferably from about 0.1 to about 0.15%, by weight of the composition, of agar or xanthan polysaccharide, which is also called xanthan gum. Xanthan gum is produced by fermentation and
15 extraction of the naturally occurring plant bacteria, Xanthomonas campestris.

E. Fatty Acid

Preferred compositions for the second type of high nonionic surfactant composition comprise from about 0.5 to about 3.5%,
20 preferably from about 1 to about 3%, most preferably from about 1.5 to about 2.5%, by weight of the composition, of C10-16, preferably C10-12, fatty acid. Preferred are lauric acid, myristic acid, palmitic acid, and stearic acid. Most preferred is lauric acid. These low levels of fatty acid are included for
25 product phase stability.

F. Other Parameters

The present aqueous laundry detergent compositions do not comprise a stability enhancing polymer which is a copolymer of a hydrophobic and a hydrophilic monomer. The second type of
30 composition (high nonionic surfactant) preferably does not include such a copolymer. Stability enhancing polymers in general need not be included herein.

The following are preferably not included in the present compositions: enzymes, an effective amount of detergency builder, urea, and glycerol. An effective amount of detergency builder is
35 preferably more than about 4% and less than about 30%, by weight

about 6, preferably from about 3.5 to about 5, most preferably from about 4 to about 4.5, and upon dilution of the composition produces a pH of between about 7 and about 10, preferably from about 7.5 to about 9, in the dilute solution.

5 1. Borate/Polyol pH Jump System

Preferably, compositions of the present invention comprise from about 2 to about 40%, preferably from about 5 to about 30%, most preferably from about 10 to about 25%, by weight of the composition, of a pH jump system comprising:

- 10 1. a borate and;
2. a polyol wherein the polyol is a cis 1,2 polyol capable of forming a complex with the borate when the composition is in a concentrated form to cause a reduction in pH of the composition to a value of about 3-6 and the complex being capable
- 15 upon dilution of the composition, of dissociating in dilute solution to liberate the borate to cause an increase in pH in the solution to a value of about 7-9, the polyol to borate weight ratio being 1:1 to 10:1.

The present compositions most preferably comprise from about

20 1 to about 20%, preferably from about 2 to about 10%, by weight of the composition, of a boron compound such as borax (preferred), boric oxide, or sodium ortho- or pyro-borate; and from about 1 to about 20%, preferably from about 5 to about 15%, by weight of the composition, of a polyol such as sorbitol, dulcitol, xylitol,

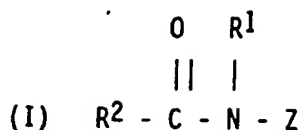
25 fructose, arabitol, mannitol, galactitol, catechol, pinacol, glucose and polyhydroxy fatty acid amide. Preferred polyols for use herein are sorbitol, xylitol and dulcitol. Most preferred compositions comprise from about 4 to about 6%, by weight of the composition, of borax and from about 10 to about 15%, by weight of

30 the composition, of sorbitol.

Preferably, the polyol is dissolved in part of the water to be added to the formula, followed by the addition to this mixture of any salt or electrolytes in the formula. Last, the boron compound is mixed into this pre-mix. This clear pH jump solution

35 is added to the remainder of the formula after the surfactants.

The mechanism of action of this borate-polyol system is believed to be the formation of an acidic borate-polyol complex in



wherein: R^1 is C_1 - C_4 hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl, or a mixture thereof, preferably C_1 - C_4 alkyl, more preferably C_1 or C_2 alkyl, most preferably C_1 alkyl (i.e., methyl); and R^2 is a C_5 - C_{31} hydrocarbyl, preferably straight chain C_7 - C_{19} alkyl or alkenyl, more preferably straight chain C_9 - C_{17} alkyl or alkenyl, most preferably straight chain C_{11} - C_{15} alkyl or alkenyl, or mixtures thereof; and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxylated derivative (preferably ethoxylated or propoxylated) thereof. Z preferably will be derived from a reducing sugar in a reductive amination reaction; more preferably Z will be a glycityl. Suitable reducing sugars include glucose, fructose, maltose, lactose, galactose, mannose, and xylose. Z preferably will be selected from the group consisting of $-\text{CH}_2-(\text{CHOH})_n-\text{CH}_2\text{OH}$, $-\text{CH}(\text{CH}_2\text{OH})-(\text{CHOH})_{n-1}-\text{CH}_2\text{OH}$, $-\text{CH}_2-(\text{CHOH})_2(\text{CHOR}')(\text{CHOH})-\text{CH}_2\text{OH}$, and alkoxylated derivatives thereof, where n is an integer from 3 to 5, inclusive, and R' is H or a cyclic or aliphatic monosaccharide. Most preferred are glycityls wherein n is 4, particularly $-\text{CH}_2-(\text{CHOH})_4-\text{CH}_2\text{OH}$.

C. pH Jump System

Solid, substantially water-insoluble peroxyacids are more stable at acidic pHs while cleaning and bleaching effectiveness of liquid laundry detergents in the wash is better at alkaline pHs. Incorporation of peroxyacid bleaches in liquid laundry detergents, particularly heavy duty liquids, was therefore thought to be impractical. Attaining these different pH requirements in product and in the wash is accomplished by using a pH jump (i.e. adjusting) system to maintain product pH between about 3 and about 6 and to achieve a pH in the wash (i.e. on dilution) of between about 7 and about 10.

The present composition comprises from about 2 to about 40%, preferably from about 5 to about 30%, most preferably from about 10 to about 25%, by weight of the composition, of a pH jump system which produces a pH in the composition of between about 3 and

3. The condensation products of ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol.

5 4. The condensation products of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylenediamine.

10 5. Semi-polar nonionic surfactants are a special category of nonionic surfactants which include water-soluble amine oxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to about 3 carbon atoms; water-soluble phosphine oxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to about 3 carbon atoms; and water-soluble sulfoxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and a moiety selected from the group consisting of alkyl and hydroxyalkyl moieties of from about 1 to about 3 carbon atoms.

20 6. Alkylpolysaccharides disclosed in U.S. Patent 4,565,647, Llenado, issued January 21, 1986, having a hydrophobic group containing from about 6 to about 30 carbon atoms, preferably from about 10 to about 16 carbon atoms and a polysaccharide, e.g., a polyglycoside, hydrophilic group containing from about 1.3 to about 10, preferably from about 1.3 to about 3, most preferably from about 1.3 to about 2.7 saccharide units.

7. Fatty acid amide surfactants having the formula:

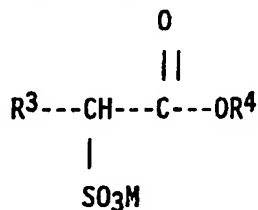


wherein R^6 is an alkyl group containing from about 7 to about 21 (preferably from about 9 to about 17) carbon atoms and each R^7 is selected from the group consisting of hydrogen, C_1 - C_4 alkyl, C_1 - C_4 hydroxyalkyl, and $-(\text{C}_2\text{H}_4\text{O})_x\text{H}$ where x varies from about 1 to about

35 The polyhydroxy fatty acid amide surfactant component comprises compounds of the structural formula:

Column 23, line 58 through Column 29, line 23 (herein incorporated by reference).

One type of anionic surfactant preferred for use in liquid detergent compositions herein is alkyl ester sulfonates, which is preferably alkyl ester sulfonate surfactant of the structural formula:



wherein R^3 is a $\text{C}_8\text{-C}_{20}$ hydrocarbyl, preferably an alkyl, or combination thereof, R^4 is a $\text{C}_1\text{-C}_6$ hydrocarbyl, preferably an alkyl, or combination thereof, and M is a soluble salt-forming cation. Suitable salts include metal salts such as sodium, potassium, and lithium salts. Preferably, R^3 is $\text{C}_{10}\text{-C}_{16}$ alkyl, and R^4 is methyl, ethyl or isopropyl. Especially preferred are the methyl ester sulfonates wherein R^3 is $\text{C}_{14}\text{-C}_{16}$ alkyl.

Preferred for use in liquid detergent compositions herein is $\text{C}_9\text{-C}_{20}$ linear alkylbenzene sulfonate (preferably sodium salts).

Preferably the nonionic surfactant is the condensation product of $\text{C}_{10}\text{-C}_{20}$ alcohol and between about 2 and about 20 moles of ethylene oxide per mole of alcohol ("E2-20 ethoxylated $\text{C}_{10}\text{-C}_{20}$ alcohol").

2. Nonionic Surfactant

Suitable nonionic detergent surfactants are generally disclosed in U.S. Patent 3,929,678, Laughlin et al., issued December 30, 1975, at column 13, line 14 through column 16, line 6, incorporated herein by reference. Exemplary, non-limiting classes of useful nonionic surfactants are listed below.

1. The polyethylene, polypropylene, and polybutylene oxide condensates of alkyl phenols

2. The condensation products of aliphatic alcohols with from about 1 to about 25 moles of ethylene oxide. The alkyl chain of the aliphatic alcohol can either be straight or branched, primary or secondary, and generally contains from about 8 to about 22 carbon atoms.

Preferably, the present compositions comprise ethoxylated nonionic surfactant:anionic surfactant in a ratio of between about 1:1 and about 30:1, preferably between about 2:1 and about 20:1, most preferably between about 2:1 and about 4:1.

5 These are preferably selected from the group consisting of C₉-20 linear alkylbenzene sulfonate, C₈-18 alkenyl carboxysulfonate, E₂-20 ethoxylated C₁₀-20 alcohols, polyhydroxy fatty acid amide, and mixtures thereof. More preferred are C₁₀-14 linear alkylbenzene sulfonate (most preferred), and E₂-5
10 ethoxylated C₁₂-18 alcohols.

1. Anionic Surfactant

Anionic surfactants useful for deterative purposes are included in the compositions hereof. These can include salts of soap, C₉-C₂₀ linear alkylbenzenesulphonates, C₈-C₂₂ primary or
15 secondary alkanesulphonates, C₈-C₂₄ olefinsulphonates, sulphonated polycarboxylic acids prepared by sulphonation of the pyrolyzed product of alkaline earth metal citrates, e.g., as described in British Patent Specification No. 1,082,179, alkyl glycerol sulfonates, fatty acyl glycerol sulfonates, paraffin sulfonates,
20 alkyl phosphates, isothionates such as the acyl isothionates, N-acyl taurates, fatty acid amides of methyl tauride, alkyl succinamates and sulfosuccinates, monoesters of sulfosuccinate (especially saturated and unsaturated C₁₂-C₁₈ monoesters) diesters
25 of sulfosuccinate (especially saturated and unsaturated C₆-C₁₄ diesters), N-acyl sarcosinates (the nonionic nonsulfated compounds being described below), branched primary alkyl sulfates, alkyl polyethoxy carboxylates such as those of the formula $RO(CH_2CH_2O)_kCH_2COO^-M^+$ wherein R is a C₈-C₂₂ alkyl, k is an integer from 0 to 10, and M is a soluble salt-forming cation, and fatty
30 acids esterified with isothionic acid and neutralized with sodium hydroxide. Resin acids and hydrogenated resin acids are also suitable, such as rosin, hydrogenated rosin, and resin acids and hydrogenated resin acids present in or derived from tall oil. Further examples are given in "Surface Active Agents and
35 Detergents" (Vol. I and II by Schwartz, Perry and Berch). A variety of such surfactants are also generally disclosed in U.S. Patent 3,929,678, issued December 30, 1975 to Laughlin, et al. at

peroxide. The reaction product is quenched by addition to ice water followed by filtration, washing with distilled water, and final suction filtration to recover the wet cake. Washing can be continued until the pH of the filtrate is neutral.

5 Preferred NAPAA is thermally annealed (or thermally agglomerated), meaning that it has been heated up to 70°C and then quenched and filtered.

Also suitable for use herein are phthaloyl aminoperoxycaproic acids ("PAP"), which are described in U.S. Patent 5,073,285, 10 Liberati et al, issued December 17, 1991, incorporated herein by reference.

Particulate (solid), organic peroxyacids with a theoretical AvO (available oxygen) of between about 3 and about 15, most preferably between 5 and 12, are preferred.

15 **B. Detergent Surfactant**

The present composition comprises, by weight of the composition, from about 5 to about 50%, preferably from about 10 to about 40%, most preferably from about 15 to about 30%, of detergent surfactant, preferably nonionic and/or anionic 20 surfactant.

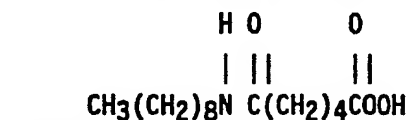
Preferred compositions for the second, high nonionic surfactant type of composition with phase stability comprise from about 10 to about 40%, preferably from about 12 to about 30%, most preferably from about 15 to about 20%, by weight of the 25 composition, of C8-20 alcohol which has been ethoxylated with an average of from about 2 to about 20 moles of ethylene oxide per mole of alcohol; and from 0 to about 10%, preferably from about 5 to about 8%, of bleach-compatible anionic surfactant.

More preferred is C10-18 alcohol which has been ethoxylated 30 with an average of from about 4 to about 15, more preferably from about 6 to about 12, moles of ethylene oxide per mole of alcohol. Blends of C10-18 alkyl ethoxylates and C10-18 alkyl ethoxylates with additional detergent surfactants, are also included herein. Most preferred is C12-15 alkylethoxylate (E6-9), which is C12-15 35 alcohol which has been ethoxylated with an average of 6-9 moles of ethylene oxide per mole of alcohol. The most preferred anionic surfactant is C12 linear alkylbenzene sulfonic acid.

Also preferred are peroxyfumarates, which are described in U.S. Patent 4,852,989, Burns et al, issued August 1, 1989, incorporated herein by reference, and sulfone peroxyacids (sulfone peroxydicarboxylic acids), which are described in U.S. Patents 4,758,369, 4,824,591, and 5,004,558, all Dryoff et al, issued July 19, 1988, April 25, 1989, and April 2, 1991, respectively, all incorporated herein by reference.

The most preferred amidoperoxyacids are monononylamido peroxyadipic acid (NAPAA; most preferred), monononylamido peroxy succinic acid (NAPSA), and 1,12-diperoxy-dodecanedioic acid (DPDA).

Another name for NAPAA is 6-(nonylamino)-6-oxo-caproic acid. The chemical formula for NAPAA is:



The molecular weight of NAPAA is 287.4.

Example I of U.S. Patent 4,686,063 (incorporated herein by reference) contains one description of the synthesis of NAPSA, from column 8, line 40 to Column 9, line 5, and NAPAA, from column 9, line 15 to column 9, line 65. At the end of the amidoperoxyacid synthesis, the reaction is quenched with water, filtered, washed with water to remove some excess sulfuric acid (or other strong acid with which the peroxyacid was made), and filtered again.

The amidoperoxyacid wet cake thus obtained can be contacted with a phosphate buffer solution at a pH between about 3.5 and 6, preferably between about 4 and 5, according to U.S. Patent 4,909,953, Sadłowski et al, issued March 20, 1990, which is incorporated herein by reference. Also incorporated by reference is U.S. Patent 5,055,218, Getty et al, issued October 8, 1991, which describes bleach granules containing amidoperoxyacid.

NAPAA filter cake herein is preferably washed twice in phosphate buffer. It has been found that two successive phosphate buffer washes lend optimal stability to NAPAA.

NAPAA can be prepared by, for example, first reacting NAAA (monononyl amide of adipic acid), sulfuric acid, and hydrogen

DESCRIPTION OF THE INVENTION

The compositions according to the present invention are aqueous and preferably comprise, by weight of the composition, from about 30 to about 70%, preferably from about 40 to about 60%, of water, preferably distilled and deionized, and from about 30 to about 70%, preferably from about 40 to about 60%, of active ingredients.

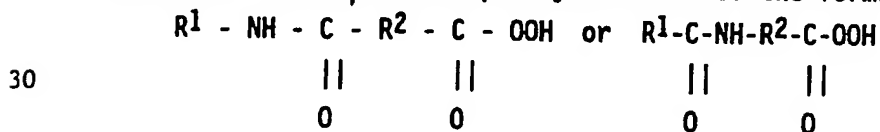
A. Peroxyacid

Compositions of the present invention comprise from about 0.5 to about 30%, preferably from about 1 to about 20%, most preferably from about 1.5 to about 5%, by weight of the composition, of solid, substantially water-insoluble organic peroxyacid.

The organic peroxyacid should be evenly suspended throughout the liquid detergent composition.

The following organic peroxyacids (IUPAC names) are preferred: 4-nonylamino-4-oxoperoxybutyric acid ("NAPSA"); 6-nonylamino-6-oxoperoxyhexanoic acid ("NAPAA"); 1,12-diperoxy-dodecanedioic acid, ("DPDA"); heptyl sulfonylperpropionic acid; decylsulphonyl perpropionic acid; heptyl-, octyl-, nonyl-, and decyl-sulphonylperbutyric acid; and phthaloyl aminoperoxycaproic acid.

Of the organic peroxyacids, amidoperoxyacids (amide substituted peroxycarboxylic acids) are preferred. Suitable amidoperoxyacids for use herein are described in U.S. Patents 4,634,551 and 4,686,063, both Burns et al, issued January 6, 1987 and August 11, 1987, respectively, both incorporated herein by reference. Suitable amidoperoxyacids are of the formula:



wherein R¹ is an alkyl group containing from about 6 to about 12 carbon atoms, and R² is an alkylene containing from 1 to about 6 carbon atoms. Preferably, R¹ is an alkyl group containing from about 8 to about 10 carbon atoms, and R² is an alkylene group containing from about 2 to about 4.

performance, product viscosity often increases to unacceptable levels.

It has now been found that a stable, pourable aqueous liquid laundry detergent composition can be formulated by including from about 0.05 to about 2 weight % of xanthan polysaccharide for phase stability, along with a specific pH jump system for cleaning performance and product bleach stability, in a peroxyacid-containing suspension. This is accomplished without the use of a stability enhancing polymer which is a copolymer of a hydrophobic and a hydrophilic monomer.

It has also been found that for improved cleaning performance without adversely affecting product viscosity, ethoxylated nonionic surfactant can be added (to the above composition containing peroxyacid and xanthan polysaccharide) in an amount greater than or equal to the amount of anionic surfactant to achieve a stable, pourable aqueous liquid detergent composition which cleans and bleaches quite well (even in the absence of enzymes and an effective amount of detergency builder). In this second type of high nonionic composition with product stability and good detergency, certain low levels of fatty acid are also included for phase stability.

SUMMARY OF THE INVENTION

This relates to a stable, pourable aqueous liquid laundry detergent composition, comprising, by weight of the composition:

- a. from about 1 to about 30% of solid, substantially water-insoluble organic peroxyacid;
- b. from about 5 to about 50% of detergent surfactant;
- c. from about 2 to about 40% of a pH jump system which produces a pH in the composition of between about 3 and about 6, and upon dilution of the composition produces a pH of between about 7 and about 10;
- d. from about 0.05 to about 2% of agar or xanthan polysaccharide; and which laundry detergent composition does not comprise a stability enhancing polymer which is a copolymer of a hydrophobic and a hydrophilic monomer.

STABLE, POURABLE AQUEOUS LIQUID LAUNDRY DETERGENT
COMPOSITIONS WITH PEROXYACID BLEACH

Josephine L. Kong-Chan
Shupef R. Chiao

5

TECHNICAL FIELD

10 This relates to stable, pourable aqueous liquid laundry detergents containing solid, substantially water-insoluble organic peroxyacid, detergent surfactant, agar or xanthan polysaccharide, and a pH jump system.

BACKGROUND OF THE INVENTION

15 U. S. Patents 4,992,194 and 5,073,285, both Liberati et al, issued February 12, 1991 and December 17, 1991, respectively, describe aqueous structured heavy duty liquid detergent formulations which contain solid, particulate, substantially water-insoluble organic peroxyacid, surfactant combinations, pH adjusting systems, and selected decoupling polymers.

20 U. S. Patent 4,879,057, Dankowski et al, issued November 7, 1989 discloses aqueous bleaching suspensions including peroxycarboxylic acid suspended in a carrier liquid in the presence of an organic thickening agent and of an acidifying agent. The suspensions contain agar or xanthan polysaccharide as thickening agent, and a hydrate-forming neutral salt.

25 Aqueous liquid laundry detergent products which contain suspended solids such as solid, substantially water-insoluble peroxyacid can have phase stability problems, particularly across the varying environmental temperatures to which such products may be exposed.

30 A further problem is product and wash pH, since low product pH is required for bleach stability while alkaline wash pH is advantageous for cleaning and bleaching efficacy (see U.S. Patent 4,259,201, Cockrell).

35 Lastly, when product detergent surfactant levels are increased in such compositions for better cleaning and bleaching

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(71) Applicant(s)

The Procter & Gamble Company

(Incorporated in USA - Ohio)

**One Procter & Gamble Plaza, Cincinnati, Ohio 45202,
United States of America**

(72) Inventor(s)

**Josephine Kong-Chan
Shupe Raymond Chiao**

(74) Agent and/or Address for Service

**Tony Nicholas Gibson
Procter & Gamble Limited, P O Box Forest Hall No 2,
Whitley Road, Longbenton, NEWCASTLE UPON
TYNE, NE12 9TS, United Kingdom**

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D165 D166 D167 D168 D169 D170 D171 D173 D182
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US 4992194 A US 4879057 A

(58) Field of Search

**UK CL (Edition M) C5D DHC DHX DHZ
INT CL⁵ C11D 3/382 3/39
On-line databases: WPI**

(54) **Stable pourable aqueous liquid detergent**

(57) **Stable, pourable aqueous liquid laundry detergents containing solid, substantially water-insoluble organic peroxyacid, detergent surfactant, agar or xanthan polysaccharide, and a pH jump system. A second type of composition also contains fatty acid and specified amounts and ratios of C8-C20 alkyl polyethoxylate for good cleaning and bleaching.**

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